Collapse of Randomly Linked Polymers

In a recent Letter, Bryngelson and Thirumalai (BT) [1] consider an ideal (i.e., non-self-interacting) polymer in which $M$ randomly chosen pairs of monomers are constrained to be in close proximity. The unconstrained chain of $N$ monomers is expanded, with a typical radius scaling as $R \approx \sqrt{N}$. By comparing variational estimates to the free energies of expanded and collapsed states, BT argue that increasing the number of (uncorrelated) links causes the polymer to collapse into a localized state in which $R$ is independent of $N$. From Eq. (10) in Ref. [1] it follows that for a generic set of constraints, where the distance (along the backbone) between linked monomers is of the order $N$, a constraint density $A/\ln N$ creates a collapsed state for sufficiently large $A$.

Here, we demonstrate that the polymer remains expanded unless $M \sim N$. We derive an exact lower bound to the squared end-to-end distance, $r^2 > N/M$, which proves that, contrary to the conclusion of BT, uncorrelated links do not cause the polymer to collapse. Numerical simulations are also performed by exploiting an analogy to random resistor networks [2]: $r^2$ equals the resistance of a chain of uniform resistivity in which randomly chosen pairs of points are connected by shorts of zero resistance. Elimination of series and parallel resistors reduces the resistance of a chain of uniform resistivity in which randomly chosen pairs of points are connected by shorts of zero resistance. Every point on this figure represents an average over 1600 randomly linked chains. The numerical results gradually converge to a slope of $-1$, as depicted by the solid line. A least squares fit to all points of the figure produces a slope 0.97, and the curve cannot be fitted as $\ln M/M$. In fact, we conclude that $r^2 = 1.5N/M$, with a prefactor that is surprisingly close to the value of 1 which appears in our simple lower bound. Details of the numerical algorithm, as well as a discussion of implications for self-avoiding polymers appear in a companion paper [3].

After completion of this work, we became aware of a work by Solf and Vilgis [4]. Although they consider more general polymer networks, their results also agree with the above findings.

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